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(54) Title: MODIFIED POLY(MALEIC ANHYDRIDE-CO-STYRENE) AND RELATED POLYMERS AS A BASE FOR COLOR FILTERS			
(57) Abstract A method of producing color elements, for use in color filter arrays and the like, and a material for use in such methods, is disclosed. The material may be a modified poly(maleic anhydride-co-styrene) and related polymers. The polymers may be used as vehicles in a clear or partially clear form, as protective or blocking and anti-leach/stain coatings. The polymers may also be combined with dyes to produce the respective color elements. The materials are compatible with conventional photolithographic methods.			

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**MODIFIED POLY(MALEIC ANHYDRIDE-CO-STYRENE) AND RELATED
POLYMERS AS A BASE FOR COLOR FILTERS**

5 Technical Field

 This invention relates generally to
polymeric materials for use in information
display devices and sensors where the coatings
contain an organic colorant to selectively pass
10 (or reject) a band of frequencies in the
ultra-violet (uv), visible, or infrared (ir)
portion of the electromagnetic spectrum, and
to optically transparent barrier coatings
providing leach/stain resistance.

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Background Art

 Production of color flat-panel displays
and color video detectors relies on the use of
colored polymeric coatings (referred to
20 hereafter as color filters) to construct an
array of colored pixels, usually red, green,
and blue for flat-panel displays and cyan,
magenta, and yellow for color video detectors.
In flat-panel displays the color filters are
25 arranged in a pattern on a transparent
substrate to allow selective passage of light
from a light source positioned behind the color
filter array. Color video detectors use color
filter arrays to pass ambient light of
30 predetermined wavelengths to an addressed array
of semiconductor photo-cells positioned behind
the color filter array.

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Color filter plate and color video detector production relies on the use of photolithographic processes to define the array of colored pixels. Two conventional general methods employed in patterning the pixel arrays are wet-etch (solvent etching) and dry-etch (plasma or reactive ion etching). Both methods require the color filter to be applied uniformly over the substrate to form a film, typically 1 - 2 μm thick for color filters. Application of the color filter is generally effected by a process known as spin-coating whereby the color filter solution is placed in the center of the spinning substrate and spread uniformly over the surface by centrifugal forces.

Wet-etch processing is a multi-step process typically involving 1) application of the color filter, 2) soft bake to partially insolubilize the coating, 3) application of photoresist, 4) exposure of photoresist, 5) solvent removal of exposed photoresist and underlying color filter, 6) solvent removal of remaining photoresist, 7) final cure of color filter. These steps are repeated for each additional color filter employed where subsequent color filters are applied over the previously processed color filters and patterned by selective removal as previously described.

Dry-etch processing is a multi-step process typically involving, 1) application of the color filter, 2) hard bake to cure the

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polymer, 3) application of photoresist, 4)
solvent removal of exposed photoresist, 5)
removal of remaining photoresist and areas of
color filter that are not coated with
5 photoresist using a reactive plasma.

The manufacture of a multi-colored array
necessitates coating each additional color
filter on top of the previously processed color
filters. When a color filter solution is
10 coated over a previously processed color filter
a phenomenon referred to as leaching can occur
in which the dyes in the previously processed
color filter diffuse out of the polymer matrix
into the solvent of the subsequent layer being
15 applied. Another phenomenon referred to as
staining can also take place in which the dyes
in the color filter solution being applied can
diffuse into the previously processed color
filter. Both phenomena result in intermixing
20 of the dyes which can decrease the chromaticity
of the color filters.

Applicant is aware of U.S. Patents:
U.S. Pat. No. 4,822,718,
U.S. Pat. No. 4,876,165, and
25 "Color Filters From Dyed Polyimides", W. Latham
and D. Hawley, Solid State Technology, May
1988, the disclosures of which are incorporated
by reference herein.

The effects of leaching and staining have
30 been reduced by using a polyimide precursor
(polyamic acid) as the color filter matrix
material(e.g., as described in U.S.4,876,165
and U.S. 4,822,718). The use of dyed

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polyimides as color filters is also described by W. Latham and D. Hawley in "Color Filters From Dyed Polyimides", Solid State Technology, May 1988. In accordance with Latham and
5 Hawley, dyed polyimides cured at 230° C for one hour offer substantial resistance to leaching and staining for film thicknesses of 1 to 2 μm . However, the leach and stain resistance of dyed polyimides is dependant on the dye loading,
10 i.e. the ratio of dye to polymer, the specific dye, the cure time/temperature, and the structure of the polyimide.

Polyimides used in color filters require care to manufacture consistently. As known, of
15 the major factors affecting the manufacture of polyimides include monomer purity, order of monomer addition, rate of monomer addition, reaction temperature, stir speed and time, and ambient humidity. As known, color filter
20 formulations using polyimides require careful formulation/evaluation processes to produce a product that performs within established specifications.

Polyimides used in color filters also lose
25 some of their optical clarity when heated at temperatures high enough to effect adequate cure. This loss of optical clarity is evidenced by a yellow coloration of the cured film which is believed to be due to the
30 formation of charge transfer complexes.

Polyimide based color filters also have a limited shelf-life. Polyimide precursors (polyamic acids) undergo a continuous

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association/dissociation of the amide linkage which results in variation of molecular weight with time. These variations in molecular weight can result in variations of the film thickness when coated at a given spin-speed and may require process adjustment, as known.

Disclosure of the Invention

It is therefore an object of the present invention to provide a composition capable of forming a transparent polymeric film capable of resisting staining from subsequent application of a dyed coating.

It is a further object of the present invention to provide a composition containing an organic dye capable of resisting leaching of the dye when the coating comes into contact with solvents in subsequent processing steps.

It is a further object of the present invention to provide a composition that has a longer useful shelf-life than the prior art, thereby allowing manufacture of a final product that maintains processibility within designated specifications for a longer period of time.

It is an object of this invention to provide a coating that does not leach.

It is yet another object of the present invention to provide a composition that does not stain.

It is still another object of the present invention to provide a photosensitive coating for use in information display devices and sensors.

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It is an object of the present invention to provide an optically transparent barrier coating.

5 Another object of the present invention is to provide a color filter base, for both positive and negative photolithographic processes, that has good electrical properties, including resistivity and dielectric strength.

10 An object of the present invention is to provide a brightener/color contrast transmitting film having a higher degree of clarity on all colors than the prior art. For example, the transmitting film makes a blue which is brighter than the blue of the prior art.

15 It is yet another object of the present invention to provide a composition that can be manufactured with consistent properties.

20 It is still another object of the present invention to provide a composition having a longer shelf life than conventional materials.

It is a further object of the present invention to provide a one component system.

25 It is an object of the present invention to provide a compound that can be securely adhered to glass and other substrates.

30 These and other objects are met by the present invention through combining a modified copolymer containing pendant anhydride groups and a material containing two or more reactive functional groups, capable of reacting with a carboxylic acid, into a single chemical entity, and thereby providing a polymeric

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coating with good solvent resistance, transparency, and thermal stability. In accordance with the present invention, coatings consisting of copolymers containing pendant
5 anhydride groups that have been grafted with a reactive crosslinking component and blended with a polyfunctional crosslinking component (preferably a blocked polyisocyanate), capable of reacting with a carboxylic acid, have been
10 found to exhibit good transparency, thermal stability, solvent resistance, leach resistance, and stain resistance.

A more complete understanding of the invention will be apparent to those skilled in
15 the art by reference to the Drawings and Description of the Preferred Embodiments incorporated herein.

Brief Description of the Drawings

20 FIG. 1 is a chart demonstrating the leach resistance of color filter elements incorporating the invention;

FIG. 2 is a chart demonstrating the leach resistance of an alternative color set
25 incorporating the invention;

FIG. 3 is a flow chart showing preparation of test color wheels incorporating the invention;

30 FIG. 4 is a chart showing staining of conventional coatings of the prior art;

FIG. 5 is a chart showing the protective effect of clear coatings incorporating the invention;

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FIG. 6 is a flow chart showing preparation and use of a clear coating according to the invention;

5 FIG. 7 is a chart showing the protective effect of using a clear photosensitive coating according to one embodiment of the invention;

FIG. 8 is a chart showing the staining and leach resistance of coatings protected by a clear coating according to the
10 invention;

FIG. 9 is a chart showing the leach resistance provided by a clear photosensitive coating according to one embodiment of the invention;

15 FIG. 10 is a chart similar to FIG. 9 using a thinner protective coating;

FIG. 11 is a flow chart showing a conventional color system according to the prior art; and

20 FIG. 12 is a flow chart showing preparation of a color system according to the invention.

Best Mode for Carrying Out the Invention

25 In accordance with the present invention, transparent polymeric coating materials with leach and stain resistance can be prepared by reacting certain copolymers which contain pendant anhydride groups, such as poly(maleic
30 anhydride-co-styrene), e.g., available under the trade name "SMA® Resins" from Atochem Inc. and under the tradename "Scripset® Resins" from Monsanto Company, and also available from

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Aldrich and Monomer-Polymer Dajac Labs,
poly(maleic anhydride-co-methylvinyl ether),
e.g., available under the tradename "Gantrez®
AN Copolymer" from ISP Technologies, or
5 poly(maleic anhydride-co-ethylene), e.g.,
available from Zeeland Chemicals Inc.,
preferably poly(maleic anhydride-co-styrene),
with a polyfunctional component having one
functional group capable of reaction with the
10 anhydride and one or more functional groups
that are capable of thermal, photo, or
chemically induced polymerization. The
polyfunctional component (referred to hereafter
as a reactive graft component) is preferably
15 allylamine, diallylamine, 3-amino-1-propanol
vinyl ether, allyl alcohol, 4-hydroxybutyl
vinyl ether, glycerol dimethacrylate,
2-hydroxyethyl methacrylate, or 2-hydroxyethyl
acrylate. The stoichiometry of the reactive
20 graft component with respect to the pendant
anhydrides may range from 0.5 to 1.0,
preferably 1.0. Reaction of the pendant
anhydrides with the reactive graft component
results in cleavage of the anhydride and
25 subsequent formation of a carboxylic acid(C=O
stretch, 1706-1760 cm⁻¹) and a carboxylic acid
ester(C=O stretch, 1715-1770 cm⁻¹), if the
functional group of the reactive graft
component that reacts with the anhydride is a
30 hydroxyl group, or an amide(C=O stretch,
1630-1700 cm⁻¹), if the functional group of the
reactive graft component that reacts with the
anhydride is an amino group. Let it be noted

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that the infra-red C=O stretching frequencies stated above represent typical absorption frequencies for the chemical functionalities described above, as reported in "Spectrometric Identification Of Organic Compounds",
5 Silverstein, Robert M.; Bassler, G. Clayton; Morrill, Terence C., Fourth Edition, Wiley, N.Y. The above stated infra-red absorption frequencies may be used as an indication of
10 reaction when grafting the reactive graft component onto the anhydride-containing copolymer. The carboxylic acid formed as a result of reacting a hydroxyl-containing compound or an amino-containing compound with
15 the anhydride functional group of the copolymer renders the grafted copolymers readily soluble in dilute aqueous base. The increased rate of dissolution in dilute aqueous base compared to the dissolution rate of the ungrafted copolymer
20 provides a qualitative indication of successful graft. A more quantitative measure of degree of graft is obtained by determination of acid number by titration with a base.

The grafted copolymer is then blended with
25 a crosslinking component that is capable of reacting with the pendant carboxylic acid groups, or unreacted anhydride groups, of the grafted copolymer. The crosslinking component can be a melamine based curative, e.g, such as
30 is available under the tradename Cymel® from Cytec Industries Inc., or polyfunctional isocyanates. The crosslinking component is preferably a blocked diisocyanate or more preferably, a blocked polyisocyanate. Blocked
35

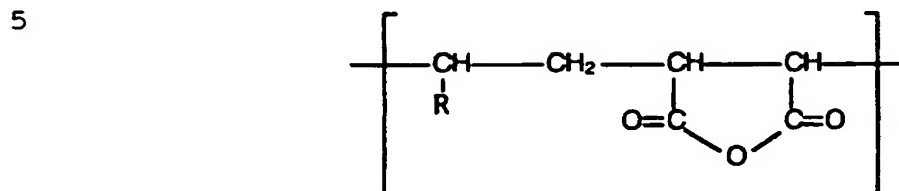
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polyisocyanates of this type are available, e.g., under the tradename "Desmodur" from Miles Inc. and under the tradename "Luxate" from Olin Chemicals. The use of blocked isocyanates permits preparation of a one part formulation with extended shelf-life since the blocked isocyanates are unreactive until heated to a predetermined temperature. Heating the blocked isocyanate to its deblock temperature generates a "free" isocyanate capable of reactions typically associated with isocyanates.

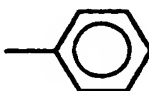
During the thermal curing process the blocked isocyanate groups begin to deblock to form free isocyanate groups at temperatures ranging from 60° C to 200° C depending on the type of blocking agent used. The free isocyanates generated in this manner then react with the carboxylic acid groups of the grafted copolymer to form an amide as described in "Organic Polymer Chemistry", K.J. Saunders, Chapman and Hall, New York, 1973. There is also the possibility of secondary reactions of the isocyanates with other functional groups containing a labile proton, such as amides, as well as reactions with other isocyanate groups. The reactions of the deblocked isocyanates described above produce extensive crosslinking of the polymer matrix. When the reactive graft component is an unsaturated alkyl group, it is also believed that at temperatures above 200°C the unsaturated bonds of the pendant reactive graft components react to provide additional crosslinking. The reactive graft component can also contain a photo-crosslinkable functionality, such as an acrylate radical.

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The structure of the starting maleic anhydride copolymer can be described, generally as follows:

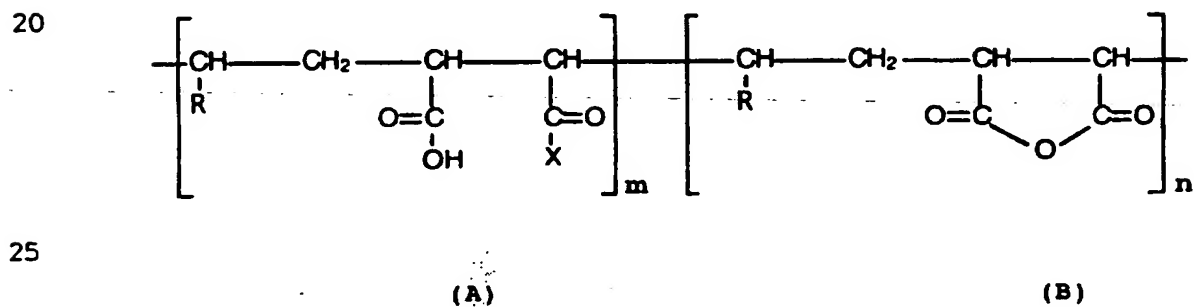


Where R = H, $-\text{OCH}_3$,



15

The structure of the grafted maleic anhydride copolymer can be described, generally as follows:

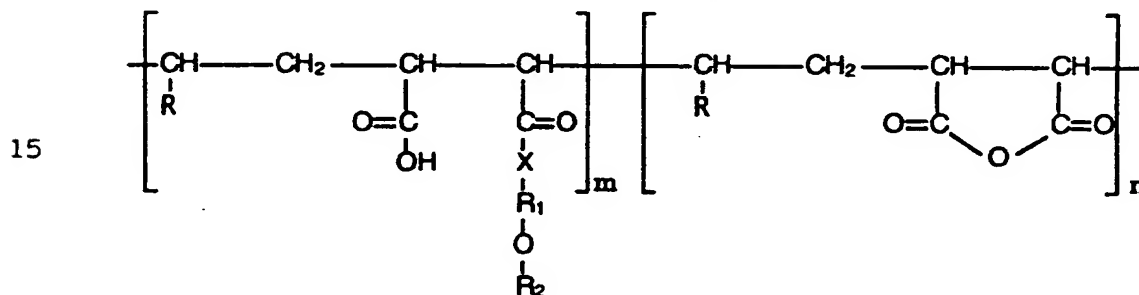


30 Where X can be a linear or branched unsaturated alcohol or amine containing from about 2 to 20 carbon atoms. Mixtures of linear or

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branched unsaturated alcohols and/or amines may also be employed.
 m can be from 0.2 to 1 and n can be from 0.8 to 0.

The moiety on the right (B) is maleic anhydride copolymer, as
 5 previously described, and the moiety on the left (A) is the grafted
 component which may contain the amine or alcohol components, as
 previously described. The substituent groups added to the
 reactive sites on the anhydride may include groups of greater
 10 complexity and functionality, for example, as follows:



20

Where X can be an oxygen atom or a nitrogen atom. R₁ is a linear
 or branched divalent alkylene of from about 1 to 6 carbon atoms or
 an oxyalkylated derivative thereof. R₂ is a vinyl, acrylate, or
 25 methacrylate radical. m can be from 0.2 to 1 and n can be from
 0.8 to 0.

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The applicants' grafted copolymer/blocked polyisocyanate blend can be applied directly to provide an optically transparent, thermally stable, chemical resistant and leach/stain resistant barrier coating with uniform coating thickness. The applicants' grafted copolymer/blocked polyisocyanate blend may also be combined with colorants to provide a uniform colored film coating possessing leach/stain resistance for use as a color filter for information displays and detectors.

Depending upon the method and the application, the applicants polymeric coating (with or without colorants) may be several microns to a few hundred Angstroms in thickness. Conventional spin-coating usually yields a film from about 0.1 μm to ten microns in thickness depending on molecular weight of the grafted copolymer and the speed at which the coating is spin-coated. Typical speeds for spin-coating the applicants polymeric coating (with or without colorants) may vary from 500 rpm to 6000 rpm depending on the type and size of substrate to be coated and the molecular weight of the copolymer and crosslinking agent used, as well as the composition of the coating. Films of greater thickness may be achieved with higher polymer solids levels and/or higher molecular weight polymer, as well as by use of other coating methods. Typical cure cycles for the applicants' polymeric coating range from 200°C to 280°C for times of 10 minutes to 60 minutes.

Some specific applications for applicants' polymeric coating include binder for dyes or

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pigments to form color filter arrays for use in liquid crystal displays, electro-luminescent displays, plasma displays and imaging systems such as charge-coupled devices for color video detectors. Applicants' polymeric coating may also be applied over coatings that lack sufficient leach/stain resistance to serve as a barrier coating to prevent staining and leaching of the aforementioned coating. Applicants' polymeric coating may also be used as an interlayer dielectric in multi-layer microcircuit fabrication. Applicants' polymeric coating may also be used in the construction of optical wave-guides.

EXAMPLE 1

Into a reaction vessel equipped with an agitator, a nitrogen inlet tube and a calcium chloride drying tube, there is charged 800 parts of N-methyl-2-pyrrolidinone and 49.8 parts allylamine. After purging the reactor with nitrogen for several minutes, 250.56 parts of styrene-maleic anhydride copolymer having a number average molecular weight of about 350,000 (Aldrich 18,293-1) and an acid number of 473 are added in a single charge while stirring. An additional 100 parts of N-methyl-2-pyrrolidinone are used to rinse the inside walls of the reactor. Stirring is continued for about 48 hours. The infra-red spectrum of the polymer shows a reduction in the intensity of the anhydride absorptions at 1858 cm^{-1} and 1780 cm^{-1} and new absorption bands at 1732 cm^{-1} and 1646 cm^{-1} corresponding to the C=O stretching vibrations of a carboxylic acid

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and a secondary amide, respectively. The product had an acid number of 157.

EXAMPLE 2

5 Into a reaction vessel equipped with an agitator, a nitrogen inlet tube and a calcium chloride drying tube, there is charged 202.23 parts of styrene-maleic anhydride copolymer having a number average molecular weight of
10 about 350,000 (Aldrich 18,293-1) and an acid number of 473 and 500 parts of N-methyl-2-pyrrolidinone. After purging the reactor with nitrogen for several minutes, the reactor is heated with an electric heating
15 mantel to a temperature 25°C to 75°C while stirring. After all solids are dissolved, the solution is allowed to cool to about 35°C. To the stirring solution there is added dropwise a solution consisting of 48.50 parts allylamine
20 in 152.78 parts N-methyl-2-pyrrolidinone. Stirring is continued at room temperature for about 48 hours. The product had an acid number of 159.

25 EXAMPLE 3

 Into a reaction vessel equipped with an agitator, a nitrogen inlet tube and a calcium chloride drying tube, there is charged 100 parts of N-methyl-2-pyrrolidinone. After
30 purging the reactor with nitrogen for several minutes, there is added 46.71 parts of styrene-maleic anhydride copolymer having a number average molecular weight of about 1600 - 2600 and an acid number of 475 (Monomer-Polymer
35 & Dajac Labs. catalog # 9182). An additional

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20 parts of N-methyl-2-pyrrolidinone are used to rinse the inside walls of the reactor. To the stirring solution there is added dropwise a solution consisting of 13.19 parts allylamine
5 in 20 parts N-methyl-2-pyrrolidinone. Stirring is continued at room temperature for about 24 hours. The product had an acid number of 144.

EXAMPLE 4

10 Into a reaction vessel equipped with an agitator, a nitrogen inlet tube and a calcium chloride drying tube, there is charged 50 parts of N-methyl-2-pyrrolidinone, 50 parts of
15 diethylene glycol dimethyl ether, and 5.87 parts allylamine. After purging the reactor with nitrogen for several minutes, 30 parts of styrene-maleic anhydride copolymer having a
20 number average molecular weight of about 350,000 (Aldrich 18,293-1) and an acid number of 473 are added to the stirring solution. A
mixture 21.74 parts of N-methyl-2-pyrrolidinone and 21.74 parts diethylene glycol dimethyl
25 ether is used to rinse the inside walls of the reactor. Stirring is continued for about 48 hours. The product had an acid number of 172.

EXAMPLE 5

Into a reaction vessel equipped with an agitator, a nitrogen inlet tube and a calcium
30 chloride drying tube, there is charged 40.44 parts of styrene-maleic anhydride copolymer having a number average molecular weight of about 350,000 (Aldrich 18,293-1) and an acid
number of 473 and 100 N-methyl-2-pyrrolidinone.
35 After purging the reactor with nitrogen for

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several minutes, a solution consisting of 8.60 parts allyl alcohol and 23.56 parts N-methyl-2-pyrrolidinone is added followed by addition of a solution of 15.00 parts triethylamine and 23.56 parts N-methyl-2-pyrrolidinone while stirring. The reaction is heated to 50°C - 65°C with an electric heating mantel. Stirring is continued for about 48 hours. The product had an acid number of 148.

EXAMPLE 6

Using the following coating formulation:
30.00 parts polymer blend consisting of 150 parts allylamine grafted styrene-maleic anhydride copolymer solution as described in Example 1, 51 parts blocked polyisocyanate (Desmodur BL-3175A, Miles Inc.), 10 parts N-methyl-2-pyrrolidinone and 25 parts cyclohexanone.

26.55	parts N-methyl pyrrolidinone
10.86	parts cyclohexanone
7.22	parts Solvent Blue 45
2.40	parts Solvent Blue 67
10	parts Dowex® HCR-S-H ion exchange resin (Dow Chemical Company)

a blue coating was prepared by stirring the mix for about 12 hours. The mix was then filtered to remove ion exchange resin and undissolved material. The coating may be used as a color filter in a multicolor pixel array for use in full-color flat-panel displays to selectively pass predominantly blue light from a light source behind the panel. The coating

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may also be used as a color filter in a multicolor pixel array to selectively pass predominantly blue light to a semiconductor photodetector array. The coating may be applied by conventional spin or spray techniques on a substrate and cured at 230°C for 60 minutes or 250°C for 30 minutes. The coating may be patterned by conventional plasma etch techniques.

EXAMPLE 7

Using the following coating formulation:

30.00	parts polymer blend as described in Example 6
26.55	parts N-methyl pyrrolidinone
10.86	parts cyclohexanone
5.61	parts Solvent Blue 38
4.03	parts Solvent Yellow 82
10	parts Dowex® HCR-S-H ion exchange resin (Dow Chemical Company)

a green coating was prepared, as described in Example 6.

EXAMPLE 8

Using the following coating formulation:

30.00	parts polymer blend as described in Example 6
26.55	parts N-methyl pyrrolidinone
10.86	parts cyclohexanone
4.50	parts Solvent Yellow 82
5.13	parts Solvent Red 119
10	parts Dowex® HCR-S-H ion exchange resin (Dow Chemical Company)

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Company)

a red coating was prepared, as described in Example 6.

5 EXAMPLE 9

Using the following coating formulation:

30.00 parts polymer blend consisting
of 150 parts allylamine grafted
styrene-maleic anhydride copolymer as
described in Example 1, 75 parts blocked
polyisocyanate (Desmodur BL-4165, Miles
Inc.), 10 parts N-methyl-2-pyrrolidinone,
and 25 parts cyclohexanone.

28.42 parts N-methyl pyrrolidinone
11.30 parts cyclohexanone
7.47 parts Solvent Blue 45
2.49 parts Solvent Blue 67
10 parts Dowex® HCR-S-H ion
exchange resin (Dow Chemical
Company)

20 a blue coating was prepared, as described in
Example 6.

EXAMPLE 10

25 Using the following coating formulation:

30.00 parts polymer blend as described
in Example 9
28.42 parts N-methyl pyrrolidinone
11.30 parts cyclohexanone
5.80 parts Solvent Blue 38
4.16 parts Solvent Yellow 82
10 parts Dowex® HCR-S-H ion
exchange resin (Dow Chemical
Company)

35 a green coating was prepared, as described in

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Example 6.

EXAMPLE 11

Using the following coating formulation:

5	30.00	parts polymer blend as described in Example 9
	28.42	parts N-methyl pyrrolidinone
	11.30	parts cyclohexanone
	4.65	parts Solvent Yellow 82
10	5.31	parts Solvent Red 119
	10	parts Dowex® HCR-S-H ion exchange resin (Dow Chemical Company)

15 a red coating was prepared, as described in
Example 6.

EXAMPLE 12

Using the following coating formulation:

20	20.00	parts polymer blend consisting of 100 parts allylamine grafted styrene-maleic anhydride copolymer solution as described in Example 1, 18.5 parts blocked polyisocyanate (Desmodur
25		BL-3175A, Miles Inc.), 28.68 parts N-methyl-2-pyrrolidinone, and 51.84 cyclohexanone.
	22.06	parts N-methyl pyrrolidinone
	11.03	parts cyclohexanone
30	3.36	parts Solvent Blue 38
	10	parts Dowex® HCR-S-H ion exchange resin (Dow Chemical Company)

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a cyan coating was prepared, as described in Example 6.

5 EXAMPLE 13

Using the following coating formulation:

	20.00	parts polymer blend as described in Example 12
	17.78	parts N-methyl pyrrolidinone
10	8.89	parts cyclohexanone
	2.40	parts Solvent Red 127
	10	parts Dowex® HCR-S-H ion exchange resin (Dow Chemical Company)

15 a magenta coating was prepared, as described in Example 6.

EXAMPLE 14

Using the following coating formulation:

20	20.00	parts polymer blend as described in Example 12
	24.89	parts N-methyl pyrrolidinone
	12.44	parts cyclohexanone
	4.00	parts Solvent Yellow 82
25	10	parts Dowex® HCR-S-H ion exchange resin (Dow Chemical Company)

a yellow coating was prepared, as described in Example 6.

30

EXAMPLE 15

Using the following coating formulation:

	5.00	parts polymer blend consisting of 20.00 parts allyl alcohol grafted styrene-maleic anhydride
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5 copolymer solution as described
 in Example 5, 5.41 parts blocked
 polyisocyanate(Desmodur
 BL-3175A, Miles Inc.), 15.36
 parts N-methyl pyrrolidinone,
 and 10.00 parts diethylene
 glycol dimethyl ether
 1.00 parts N-methyl pyrrolidinone
 1.38 parts diethylene glycol dimethyl
 10 ether
 4.92 parts dye stock consisting of
 56.25 parts Solvent Blue 45,
 18.75 parts Solvent Blue 67,
 112.5 parts N-methyl
 15 pyrrolidinone, and 112.5 parts
 diethylene glycol dimethyl ether
 stirred over 64 parts Dowex®
 HCR-S-H ion exchange resin (Dow
 Chemical Company) for 12 - 24
 20 hours followed by filtration to
 remove ion exchange resin and
 undissolved materials.

a blue coating was prepared, as described in
 Example 6.

25

EXAMPLE 16

Using the following coating formulation:

5.00 parts polymer blend as described
 in Example 15
 30 1.00 parts N-methyl pyrrolidinone
 1.38 parts diethylene glycol dimethyl
 ether
 4.92 parts dye stock consisting of
 43.65 parts Solvent Blue 38,
 35 31.35 parts Solvent Yellow 82,

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- 112.5 parts
N-methyl-pyrrolidinone, and
112.5 parts diethylene glycol
dimethyl ether stirred over 64
5 parts Dowex® HCR-S-H ion
exchange resin (Dow Chemical
Company) for 12 - 24 hours
followed by filtration to remove
undissolved materials.
- 10 a green coating was prepared, as described in
Example 6.

EXAMPLE 17

- Using the following coating formulation:
- | | | |
|----|------|--|
| 15 | 5.00 | parts polymer blend as described
in Example 15 |
| | 1.00 | parts N-methyl pyrrolidinone |
| | 1.38 | parts diethylene glycol dimethyl
ether |
| 20 | 4.92 | parts dye stock consisting of
35.03 parts Solvent Yellow 82,
39.97 parts Solvent Red 119, 130
parts N-methyl-pyrrolidinone,
and 130 parts diethylene glycol
dimethyl ether stirred over 64
25 parts Dowex® HCR-S-H ion
exchange resin (Dow Chemical
Company) for 12 - 24 hours
followed by filtration to remove
undissolved materials. |
| 30 | | a red coating was prepared, as described in
Example 6. |

EXAMPLE 18

- 35 Using the following formulation:

-25-

5.50 parts grafted copolymer as
described in Example 1
1.93 parts blocked polyisocyanate
(Desmodur BL-3175A, Miles Inc.)
5 1.19 parts Solvent Blue 67
1.64 parts Solvent Brown 44
11.31 parts cyclohexanone
4.13 parts N-methyl-2-pyrrolidinone
10 10 parts Dowex HCR-S-H ion exchange
resin

a black coating was prepared, as described in
Example 6.

EXAMPLE 19

15 Using the following formulation:
6.37 parts grafted copolymer as
described in Example 1
2.17 parts blocked polyisocyanate
(Desmodur BL-3175A, Miles Inc.)
20 3.56 parts cyclohexanone
3.42 parts N-methyl-2-pyrrolidinone
a clear coating was prepared by stirring the
mix for about 1 hour. The mix was then
filtered through a 0.2 μ m filter. The coating
25 may be used as a transparent barrier layer over
color filters to provide protection against
leaching of the dyes from the color filter and
to protect against staining of the color filter
during subsequent processing steps. It will be
30 appreciated that various dyes may be added to
produce a coating which is transparent at
selected wavelengths and opaque at other
wavelengths. For example, the coating may be
transparent at the spectra used to determine
35 alignment, but opaque, or colored, at other

-26-

wavelengths.

EXAMPLE 20

The blue color filter formulation described in Example 6 was spin-coated onto a three inch diameter glass substrate at 1000 rpm for 90 seconds, baked on a hotplate at 100°C for 30 - 60 seconds, pre-baked in a convection oven at 170°C for 30 minutes, and hard-baked (cured) in a convection oven at 250°C for 30 minutes. Film thickness was 1.45 μm . The transmittance spectrum of the cured color filter film is represented by line a in Figure 1. The coated glass substrate was then immersed in N-methyl-2-pyrrolidinone for 30 seconds after which it was dried under a stream of dry nitrogen. The transmittance spectrum was recorded again and is represented by line b in Figure 1. The coated glass substrate was immersed a second time in N-methyl-2-pyrrolidinone for 30 seconds after which it was dried under a stream of dry nitrogen. The transmittance spectrum was recorded again and is represented by line c in Figure 1.

EXAMPLE 21

The green color filter formulation described in Example 7 was spin-coated onto a three inch diameter glass substrate at 1000 rpm for 90 seconds, baked on a hotplate at 100°C for 30 - 60 seconds, pre-baked in a convection oven at 170°C for 30 minutes, and hard-baked (cured) in a convection oven at 250°C for 30 minutes. Film thickness was 1.24 μm . The

-27-

transmittance spectrum of the cured color filter film is represented by line d in Figure 1. The coated glass substrate was then immersed in N-methyl-2-pyrrolidinone for 30 seconds after which it was dried under a stream of dry nitrogen. The transmittance spectrum was recorded again and is represented by line e in Figure 1. The coated glass substrate was immersed a second time in N-methyl-2-pyrrolidinone for 30 seconds after which it was dried under a stream of dry nitrogen. The transmittance spectrum was recorded again and is represented by line f in Figure 1.

EXAMPLE 22

The red color filter formulation described in Example 8 was spin-coated onto a three inch diameter glass substrate at 1000 rpm for 90 seconds, baked on a hotplate at 100°C for 30 - 60 seconds, pre-baked in a convection oven at 170°C for 30 minutes, and hard-baked (cured) in a convection oven at 250°C for 30 minutes. Film thickness was 1.36 μm . The transmittance spectrum of the cured color filter film is represented by line g in Figure 1. The coated glass substrate was then immersed in N-methyl-2-pyrrolidinone for 30 seconds after which it was dried under a stream of dry nitrogen. The transmittance spectrum was recorded again and is represented by line h in Figure 1. The coated glass substrate was immersed a second time in N-methyl-2-pyrrolidinone for 30 seconds after which it was dried under a stream of dry

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nitrogen. The transmittance spectrum was recorded again and is represented by line i in Figure 1.

5 **EXAMPLE 23**

 The cyan color filter formulation described in Example 12 was spin-coated onto a three inch diameter glass substrate at 2000 rpm for 90 seconds, baked on a hotplate at 100°C
10 for 30 - 60 seconds, and hard-baked (cured) in a convection oven at 250°C for 30 minutes. Film thickness was 0.579 μm . The transmittance spectrum of the cured color filter film is represented by line a in Figure 2. The coated
15 glass substrate was then immersed in N-methyl-2-pyrrolidinone for 30 seconds after which it was dried under a stream of dry nitrogen. The transmittance spectrum was recorded again and is represented by line b in
20 Figure 2. The coated glass substrate was immersed a second time in N-methyl-2-pyrrolidinone for 30 seconds after which it was dried under a stream of dry nitrogen. The transmittance spectrum was
25 recorded again and is represented by line c in Figure 2.

EXAMPLE 24

 The yellow color filter formulation
30 described in Example 14 was spin-coated onto a three inch diameter glass substrate at 2000 rpm for 90 seconds, baked on a hotplate at 100°C for 30 - 60 seconds, and hard-baked (cured) in a convection oven at 250°C for 30 minutes. Film
35 thickness was 0.585 μm . The transmittance

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spectrum of the cured color filter film is represented by line d in Figure 2. The coated glass substrate was then immersed in N-methyl-2-pyrrolidinone for 30 seconds after which it was dried under a stream of dry nitrogen. The transmittance spectrum was recorded again and is represented by line e in Figure 2. The coated glass substrate was immersed a second time in N-methyl-2-pyrrolidinone for 30 seconds after which it was dried under a stream of dry nitrogen. The transmittance spectrum was recorded again and is represented by line f in Figure 2.

EXAMPLE 25

The magenta color filter formulation described in Example 13 was spin-coated onto a three inch diameter glass substrate at 2000 rpm for 90 seconds, baked on a hotplate at 100°C for 30 - 60 seconds, and hard-baked (cured) in a convection oven at 250°C for 30 minutes. Film thickness was 0.708 μm . The transmittance spectrum of the cured color filter film is represented by line g in Figure 2. The coated glass substrate was then immersed in N-methyl-2-pyrrolidinone for 30 seconds after which it was dried under a stream of dry nitrogen. The transmittance spectrum was recorded again and is represented by line h in Figure 2. The coated glass substrate was immersed a second time in N-methyl-2-pyrrolidinone for 30 seconds after which it was dried under a stream of dry nitrogen. The transmittance spectrum was

-30-

recorded again and is represented by line i in Figure 2.

EXAMPLE 26

5 Using the following formulation:
 6.37 parts grafted copolymer as
 described in Example 1
 2.17 parts blocked polyisocyanate
 (Desmodur BL-3175A, Miles Inc.)
10 3.56 parts cyclohexanone
 3.42 parts N-methyl-2-pyrrolidinone
a clear coating was prepared by stirring the
mix for about 1 hour. The mix was then
filtered through a 0.2 μ m filter. The coating
15 may be used as a transparent barrier layer over
color filters to provide protection against
leaching of the dyes from the color filter and
to protect against staining of the color filter
during subsequent processing steps.

20

EXAMPLE 27

Evaluation of the stain resistance of the
formulation of Example 25 was conducted by
preparing a three-color color wheel on a three
25 inch diameter glass substrate, as illustrated
in Figure 3, that simulates the processing
steps used in preparing a color filter plate.
The steps used in preparing the color wheel are
as follows:

30 1) Spin-coat clear barrier coat of
example 25 at 1220 rpm for 90 seconds, bake on
hotplate at 100°C for 30 - 60 seconds, bake in
convection oven at 250°C for 60 minutes. Film
thickness was 1.1 μ m. Spectra of clear coat
35 after this step is shown in Figure 4, line a.

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- 2) Spin-coat red color filter (Brewer Science, Inc. Pic[®] Red 101) at 1200 rpm for 90 seconds, bake on hotplate at 100°C for 30 - 60 seconds, bake in convection oven at 164°C for 30 minutes.
- 3) Spin-coat positive working photoresist (Shipley Microposit[®] 1400-27) at 5000 rpm for 30 seconds, hotplate bake at 100°C for 30 seconds.
- 4) The sample was then exposed to actinic light (150 mJ/cm²) from a contact printer through a wedge-shaped mask placed over the coated substrate.
- 5) The sample was immersed in 0.27 N tetramethylammonium hydroxide (TMAH) for 20 seconds followed by rinsing in deionized water to remove exposed resist and underlying Red 101 leaving a hemi-circular pattern of Red 101. The unexposed resist remaining on top of the Red 101 was removed with SafeStrip[®] (Brewer Science, Inc.). The remaining Red 101 was then hard-baked (cured) in a convection oven at 280°C for 10 minutes. Red 101 film thickness was approximately 1.25 μ m per certificate of analysis. Spectra of the Red 101 and the clear coat after this step are shown in Figure 4, lines b and c, respectively.
- 6) Spin-coat green color filter (Brewer Science, Inc. Pic[®] Green 02) at 1200 rpm for 90 seconds, bake on hotplate at 100°C for 30 - 60 seconds, bake in convection oven at 170°C for 30 minutes. Spin-coat positive working photoresist (Shipley Microposit[®] 1400-27) at 5000 rpm for 30 seconds, hotplate bake at 100°C for 30 seconds. The sample was

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then exposed to actinic light (150 mJ/cm^2) from a contact printer through a wedge-shaped mask placed over the coated substrate and rotated 90 degrees from its position in step 4.

5 7) The sample is immersed in 0.27 N tetramethylammonium hydroxide (TMAH) for 20 seconds followed by rinsing in deionized water to remove exposed resist and underlying Green
10 02. The unexposed resist remaining on top of the Green 02 is removed with SafeStrip® (Brewer Science, Inc.). The remaining Green 02 is then hard-baked (cured) in a convection oven at
15 230°C for 60 minutes. Green 02 film thickness was approximately $1.20 \text{ }\mu\text{m}$ per certificate of analysis. Spectra of the Green 02, Red 101, and the clear coat after this step are shown in Figure 4, lines d, e, and f, respectively.

 8) Spin-coat blue color filter (Brewer
20 Science, Inc. Pic® EXP93004) at 1000 rpm for 90 seconds, bake on hotplate at 100°C for 30 - 60 seconds, bake in convection oven at 155°C for 30 minutes. Spin-coat positive working photoresist (Shipley Microposit® 1400-27) at
25 5000 rpm for 30 seconds, hotplate bake at 100°C for 30 seconds. The sample is then exposed to actinic light (150 mJ/cm^2) from a contact printer through a wedge-shaped mask placed over the coated substrate and rotated 90 degrees
30 from its position in step 6.

 9) The sample is immersed in 0.27 N tetramethylammonium hydroxide (TMAH) for 20 seconds followed by rinsing in deionized water to remove exposed resist and underlying
35 EXP93004 leaving a hemi-circular pattern of

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EXP93004. The unexposed resist remaining on top of the EXP93004 is removed with SafeStrip® (Brewer Science, Inc.). The remaining EXP93004 is then hard-baked (cured) in a convection oven at 230°C for 60 minutes. EXP93004 film thickness was approximately 1.00 μm per certificate of analysis. Spectra of the EXP93004, Green 02, Red 101, and the clear coat after this step are shown in Figure 4, lines g, h, i, and j, respectively.

In Figure 4, the slight decrease in transmittance of the clear coat, represented by lines a, c, f, and j, is a result of thermal darkening. There is no spectral evidence of staining from any of the subsequent color filter processing steps. Line g in Figure 4 shows a decrease in transmittance of the red color filter due to staining from subsequent processing of the blue color filter.

A second color wheel was prepared as described above in steps 1 - 9 with the exception that a second application of the clear coat in Example 25 was applied after processing the red color filter as described in step 5. The second application of clear coat was spin-coated at 6000 rpm for 90 seconds, baked on hotplate at 100°C for 30 - 60 seconds, and baked in convection oven at 250°C for 60 minutes. The transmittance spectrum of the clear coat and each color filter was recorded after each hard-bake as described in steps 1 - 9 for the first color wheel. Lines a - j in Figure 5 correspond to the same processing steps as lines a - j in Figure 4. Line g in Figure 5 indicates no staining of the

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red color filter by the subsequent application of the blue color filter. The slight decrease in the transmittance of the red color filter represented by line g in Figure 5 is due to thermal degradation of the dyes.

EXAMPLE 28

Into a reaction vessel equipped with an agitator, and a calcium chloride drying tube, there is charged 50.00 parts of SafeStrip® (Brewer Science, Inc.) to which is added 40.00 parts styrene-maleic anhydride copolymer having a number average molecular weight of about 1900 (Atochem SMA3000A) and an acid number of 290. After all solids are dissolved, there is added 12.00 parts 2-hydroxyethyl acrylate (HEA) (RohmTech AM-414) and 10 drops of triethylamine (Aldrich 23,962-3). Stirring is continued at room temperature for about 24 hours.

EXAMPLE 29

Into a 100 mL polyethylene beaker there is charged 29.82 parts of the grafted polymer prepared in Example 27, 5.00 parts dipentaerythritol penta-/hexa- acrylate (Aldrich 40,728-3, and 8.69 parts SafeStrip® (Brewer Science, Inc.). The mix is stirred at room temperature for 1 hour and stored in an amber polyethylene screw-cap bottle for 14 days.

EXAMPLE 30

An optical transparent negative working photoresist is prepared by combining 10.00

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parts of the formulation prepared in Example 28, 1.90 parts blocked polyisocyanate (Desmodur B1-3175A, Miles Inc), 20.00 parts SafeStrip[®], 1.00 parts isopropylthioxanthone (ITX) (First Chemical Corp.), 0.50 parts octyl-para-(dimethylamino) benzoate(ODAB) (First Chemical Corp.), and 0.025 parts 1,4-diazabicyclo[2.2.2]octane (Aldrich D2,780-2). The mix is stirred for 1 hour at room temperature and filtered through a 0.2 μ m.

EXAMPLE 31

Evaluation of the formulation of Example 29 was conducted by preparing a three-color color wheel on a three inch diameter glass substrate, as illustrated in Figure 6, that simulates the processing steps used in preparing a color filter plate. The steps used in preparing the color wheel are as follows:

- 1) Spin-coat red color filter (Brewer Science, Inc. Pic[®] Red 02) at 1000 rpm for 90 seconds, bake on hotplate at 100°C for 30 seconds, bake in convection oven at 151°C for 30 minutes.
- 2) Spin-coat transparent negative working photoresist prepared in Example 29 at 4000 rpm for 90 seconds, hotplate bake at 100°C for 3 minutes.
- 3) The sample was then exposed to actinic light (150 mJ/cm²) from a contact printer through a wedge-shaped mask placed over the coated substrate followed by baking on a hotplate at 100°C for 2 minutes.
- 4) The sample was immersed in 0.27 N tetramethylammonium hydroxide (TMAH) for 20

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seconds followed by rinsing in deionized water to remove unexposed resist and underlying Red 02 leaving a hemi-circular pattern of Red 02 with a layer of transparent resist on top. The remaining Red 02 and transparent resist were then hard-baked (cured) in a convection oven at 230°C for 30 minutes. Red 02 film thickness was approximately 1.2 μm per certificate of analysis. Transparent resist film thickness was approximately 0.35 μm . Spectrum of the Red 02 coated with the transparent resist after this step are represented by line a in Figure 7.

5) Spin-coat green color filter (Brewer Science, Inc. PiC[®] Green 02) at 1100 rpm for 90 seconds, bake on hotplate at 100°C for 30 seconds, bake in convection oven at 165°C for 30 minutes. Spin-coat transparent negative working photoresist prepared in Example 29 at 4000 rpm for 90 seconds, hotplate bake at 100°C for 3 minutes. The sample was then exposed to actinic light (150 mJ/cm²) from a contact printer through a wedge-shaped mask placed over the coated substrate and rotated 90 degrees from its position in step 3.

6) The sample was immersed in 0.27 N tetramethylammonium hydroxide (TMAH) for 20 seconds followed by rinsing in deionized water to remove unexposed resist and underlying Green 02 leaving a hemi-circular pattern of Green 02. The remaining Green 02 and transparent resist were then hard-baked (cured) in a convection oven at 230°C for 30 minutes. Green 02 film thickness was approximately 1.20 μm per certificate of analysis. Transparent resist

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film thickness was approximately 0.35 μm . Spectra of the Green 02 coated with transparent resist and Red 02 coated with the transparent resist after this step are represented by lines b and c, respectively, in Figure 7.

5 7) Spin-coat blue color filter (Brewer Science, Inc. PiC[®] Blue 10) at 1200 rpm for 90 seconds, bake on hotplate at 100°C for 30 seconds, bake in convection oven at 160°C for
10 30 minutes. Spin-coat transparent negative working photoresist prepared in Example 29 at 4000 rpm for 90 seconds, hotplate bake at 100°C for 3 minutes. The sample was then exposed to
15 actinic light (150 mJ/cm²) from a contact printer through a wedge-shaped mask placed over the coated substrate and rotated 90 degrees from its position in step 5.

 8) The sample was immersed in 0.27 N tetramethylammonium hydroxide (TMAH) for 20
20 seconds followed by rinsing in deionized water to remove unexposed resist and underlying Blue 10 leaving a hemi-circular pattern of Blue 10. The remaining Blue 10 and transparent resist were then hard-baked (cured) in a convection
25 oven at 230°C for 30 minutes. Green 02 film thickness was approximately 1.20 μm per certificate of analysis. Transparent resist film thickness was approximately 0.35 μm . Spectra of the Blue 10 coated with transparent
30 resist, Green 02 coated with transparent resist, and Red 02 coated with the transparent resist after this step are represented by lines d, e, and f, respectively, in Figure 7.

 In Figure 7, the slight decrease in
35 transmittance of the Red 02, represented by

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lines a, c, and f, and of the Green 02, represented by lines b and e, is a result of thermal darkening and some staining from any of the subsequent color filter processing steps, but the effect is minimal.

A second color wheel was prepared as described above in steps 1 - 9 with the exception that the Blue 10 was not hard-baked after development in TMAH. Instead, the color wheel was placed on the spinner and spun at 2000 rpm while being sprayed with a stream of N-methyl-2-pyrrolidinone from a squeeze bottle for approximately 10 seconds. The color wheel was allowed to spin at 2000 rpm for an additional 80 seconds to aid in drying the wheel. Figure 8 shows the spectrum of the Red 02 and Green 02 after each hard-bake and removal of Blue 10 where lines a, c, and e represent the transmittance spectra of Red 02 and lines b and d represent the transmittance spectra of Green 02. The spectra show slight decreases in transmittance for the Red 02 and the Green 02 due to thermal decomposition of the dyes. The spectra indicate that the removal of the Blue 10 with N-methyl-2-pyrrolidinone did not stain the Green 02 and Red 02 and that there was no leaching of dyes from the Green 02 and Red 02 during the Blue 10 removal step.

EXAMPLE 32

Three glass substrates, measuring three inches in diameter, were coated with a blue color filter material (EXP94056, Brewer Science, Inc.) by spin-coating at 800 rpm for

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90 seconds. Each sample was baked on a hotplate for 30 seconds. Sample 1 was baked in a convection oven at 250°C for 30 minutes, sample 2 was baked in a convection oven at 230°C for 60 minutes, and sample 3 was baked in a convection oven at 165°C for 30 minutes. Sample 2 was spin-coated with a 1:1 dilution of the transparent resist, described in Example 29, and SafeStrip® (Brewer Science, Inc.). The diluted transparent resist was spin-coated at 1000 rpm for 90 seconds, followed by a hotplate bake at 100°C for 3 minutes. The sample was flood-exposed (150 mJ/cm²) on a contact printer and placed in a convection oven at 230°C for 30 minutes. Film thickness was determined to be 0.39 μm from a spin-curve. Sample 3 was coated with the diluted transparent resist, as previously described, by spin-coating at 5000 rpm for 90 seconds, followed by a hotplate bake at 100°C for 3 minutes. The sample was flood-exposed (150 mJ/cm²) on a contact printer and placed in a convection oven at 230°C for 30 minutes. Film thickness was determined to be 0.1 μm from a spin-curve. Evaluation of solvent resistance was performed by immersing each sample in N-methyl-2-pyrrolidinone. The spectrum of each sample was recorded before and after immersion in N-methyl-2-pyrrolidinone. Sample 1 was stripped from the substrate during immersion in N-methyl-2-pyrrolidinone. Line a in Figure 9 represents the transmittance spectrum of the blue color filter of sample 2 before application of the transparent resist. Line b in Figure 9 represents the transmittance spectrum of sample 2 with the transparent

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resist baked on. Line c in Figure 9 represents the transmittance spectrum of sample 2 with the transparent resist baked on, after immersion in N-methyl-2-pyrrolidinone for 30 seconds.

5 Line a in Figure 10 represents the transmittance spectrum of the blue color filter of sample 3 after application and curing of the transparent resist. Line b in Figure 10 represents the transmittance spectrum of sample
10 3 with the transparent resist baked on, after immersion in N-methyl-2-pyrrolidinone for 30 seconds.

 While the above examples have been shown as using a separate vehicle and soluble dye, it
15 will be appreciated that the dye may be a part of the vehicle polymer, e.g. attached to the polymer as an addition compound. The polymer may also be one which has the desired filtering properties, transmitting light of a desired
20 wavelength, and excluding other wavelengths.

 It will be appreciated by those skilled in the art that variations in the invention disclosed herein may be made without departing from the spirit of the invention disclosed.
25 The invention is not to be limited by the specific embodiments disclosed herein but only by the scope of the claims appended hereto:

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Claims

1. In a process of making color filter elements by photolithography, the improvement comprising, applying a layer
5 of a substantially non-particulate filter coating material to a filter substrate, the filter coating material including a vehicle and a soluble dye incorporated therewith, the soluble dye being heat
10 stable and in combination with the vehicle being effective to produce a high color contrast and brightness at reduced levels of back light, applying a photoresist to the layer of the filter coating material
15 on the filter substrate, photographically imaging and developing the photoresist to form a pattern in the photoresist, transferring the pattern to the filter coating material by etching the patterned photoresist, to form a color filter
20 element pattern in the color filter material, curing the color filter element to substantially insolubilize the color element, the cured filter element
25 containing the stable dye being effective to consistently transmit and resolve colored light at high brightness, the cured filter element containing the stable dye having a high resistance to leaching
30 and staining from adjacent application of subsequent filters.
2. The method of claim 1 wherein the
35 substrate is coated with a substantially planar array of filter elements, the

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filter elements being of a plurality of colors.

- 5 3. The process of claim 2 including orienting
 the filter coating material in the color
 filter element to provide alignment.
- 10 4. The method of claim 3 including applying a
 liquid crystal material to the oriented
 filter coating material.
- 15 5. The method of claim 1 wherein the vehicle
 includes an anhydride modified copolymer
 grafted with a reactive crosslinking
 component and blended with a
 polyfunctional crosslinking component.
- 20 6. In a process of making microelectronic
 filter elements by microphotolithography,
 the improvement comprising applying a
 layer of a substantially non-particulate
 filter coating to a filter substrate, the
 filter coating material including a
 vehicle and a soluble dye incorporated
25 therewith, the soluble dye being heat
 stable and in combination with the vehicle
 being effective to produce a high color
 contrast and brightness at reduced levels
 of back light, forming a pattern on the
30 color filter material, and etching to form
 a color filter element, curing the color
 filter element to substantially
 insolubilize the color element, applying a
 barrier coating to the colored filter
35 element, curing the barrier coating to

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substantially insolubilize the barrier coating, the cured filter element containing the stable dye being effective to consistently transmit and resolve colored light at high brightness, the cured barrier coating providing a high resistance to leaching and staining from adjacent application of subsequent filters.

10

7. In a process of making microelectronic filter elements by microphotolithography, the improvement comprising applying a layer of a substantially non-particulate filter coating material to a filter substrate, the filter coating material including a vehicle and a soluble dye incorporated therein, the soluble dye being heat stable and in combination with the vehicle being effective to produce a high color contrast and brightness at reduced levels of back light, applying a photosensitive barrier coating to the layer of color filter coating material on the filter substrate, photographically patterning the photosensitive barrier coating and developing the pattern in the barrier coating, transferring the pattern to the filter coating material by etching to form a color filter element covered by the patterned barrier coating, curing the color filter element and barrier coating to substantially insolubilize the color filter element and barrier coating, the cured color filter element containing the

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30

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5 stable dye being effective to consistently transmit and resolve colored light at high brightness, the cured barrier coating providing a high resistance to leaching and staining from adjacent application of subsequent color filter elements.

10 8. A light absorbing coating material for photolithography including a vehicle and a soluble light absorbing dye incorporated therewith, the soluble dye being heat stable and in combination with the vehicle being effective to produce a high color contrast and brightness at reduced levels of back light, the vehicle including an anhydride modified copolymer grafted with a reactive crosslinking component and blended with a polyfunctional crosslinking component.

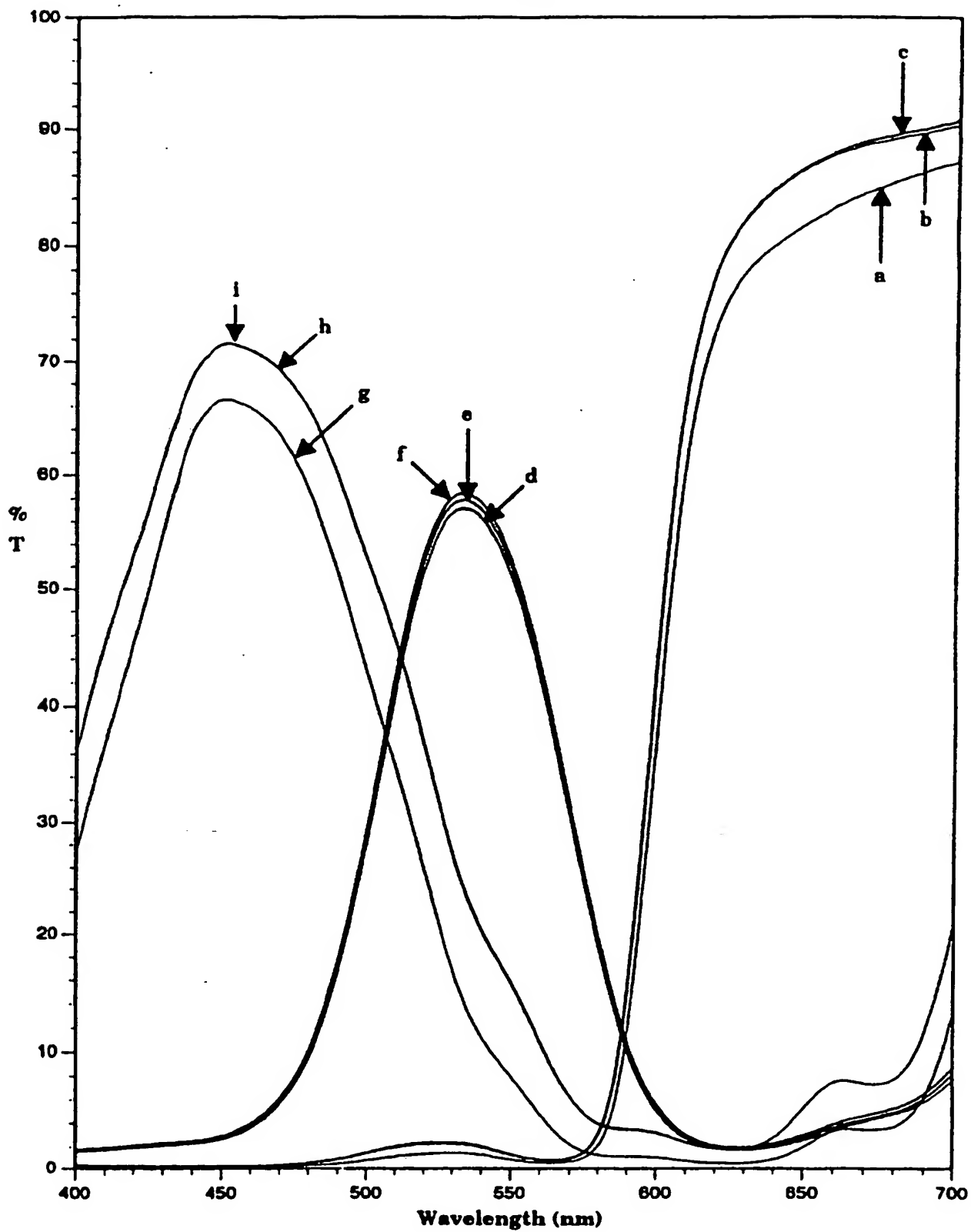
20 9. A color filter substrate having a patterned filter element thereon, the filter element including a substantially non-particulate filter coating material, the filter coating material including a vehicle and a dye incorporated therewith, the soluble dye being heat stable and in combination with the vehicle being effective to produce a high color contrast and brightness at reduced levels of back light, the filter element having a high resistance of leaching and staining from adjacent filters.

35

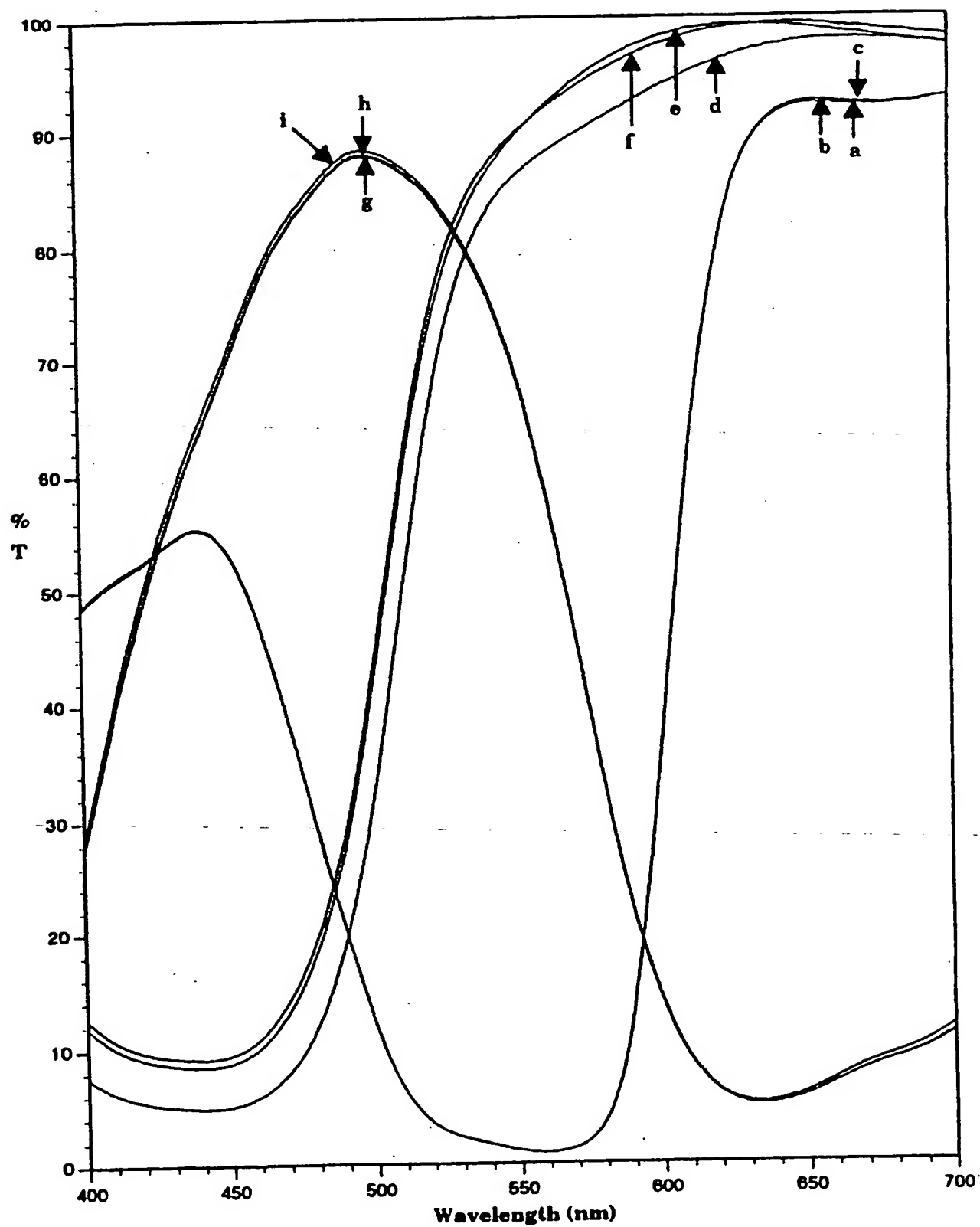
-45-

10. The filter substrate of claim 9 wherein
the vehicle includes an anhydride modified
copolymer grafted with a reactive
crosslinking component and blended with a
polyfunctional crosslinking component.
- 5

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*Fig. 1*

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*Fig. 2*

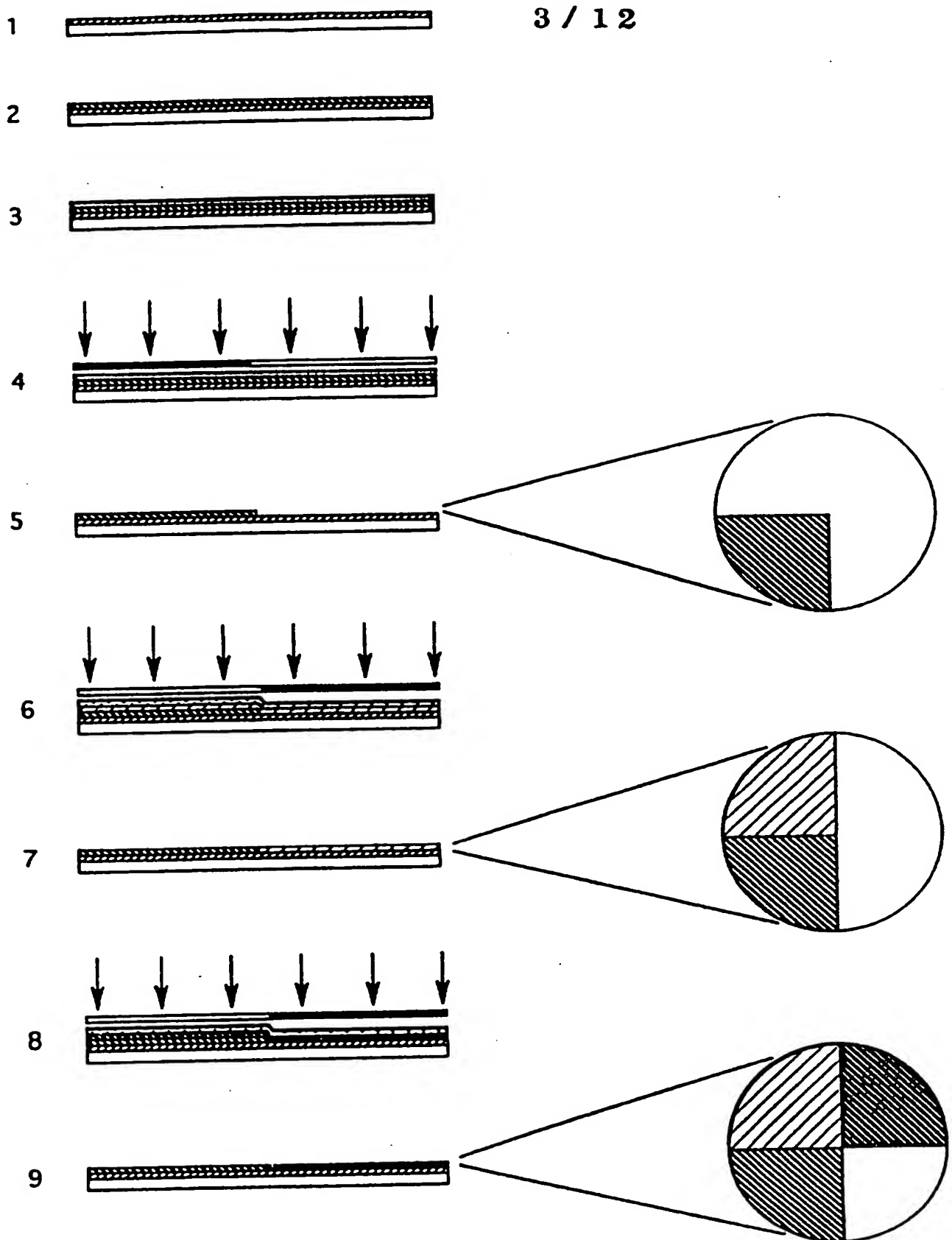
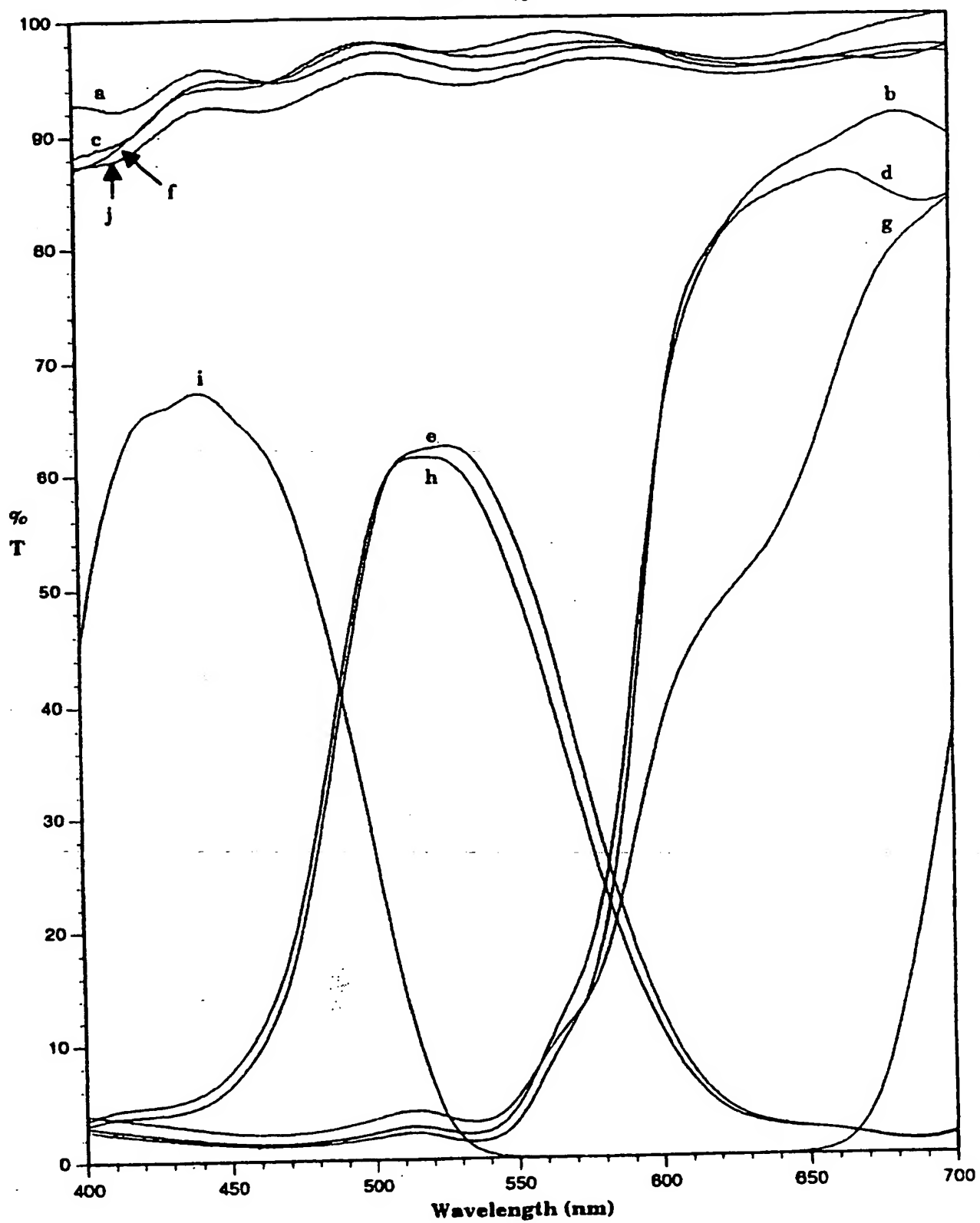
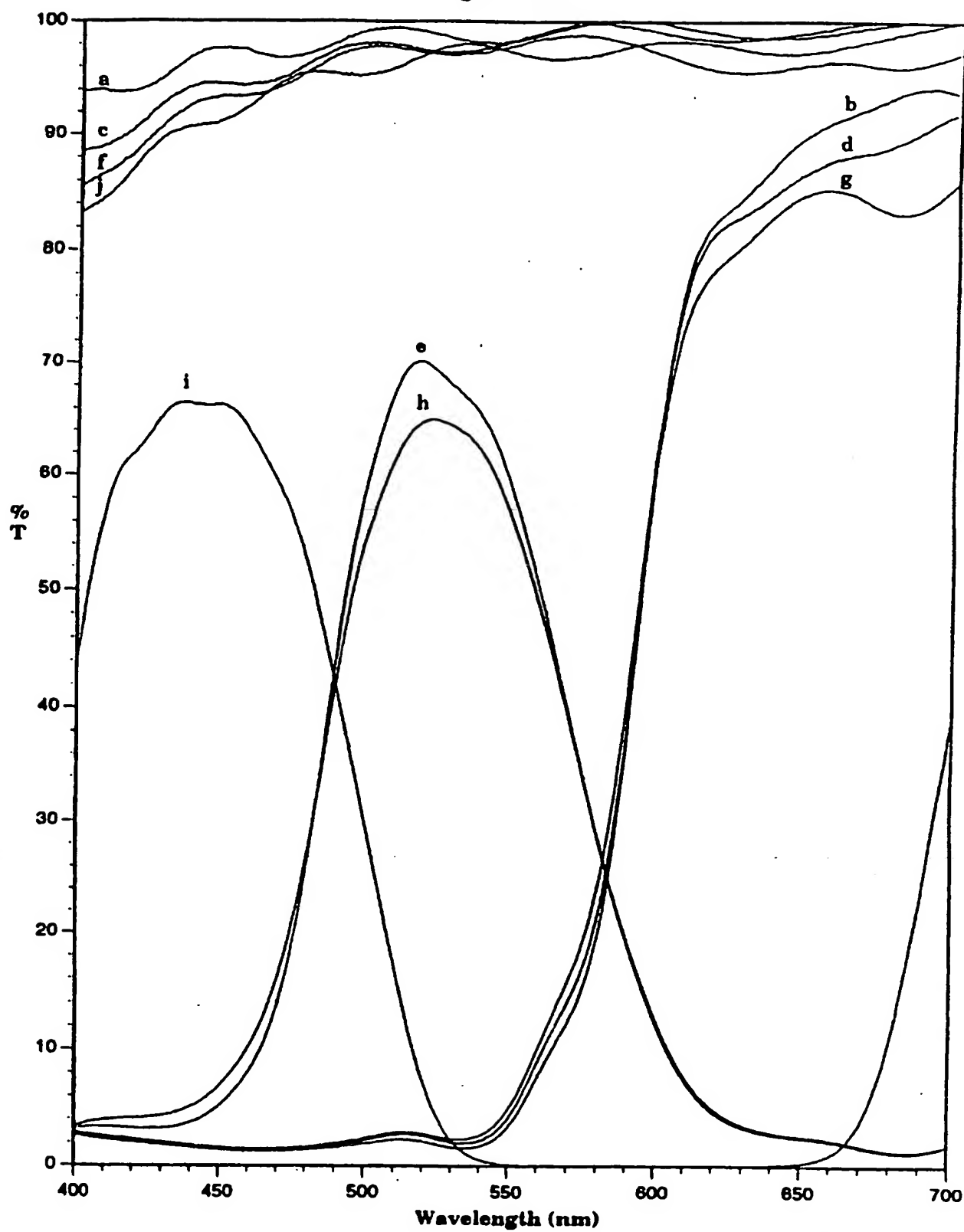


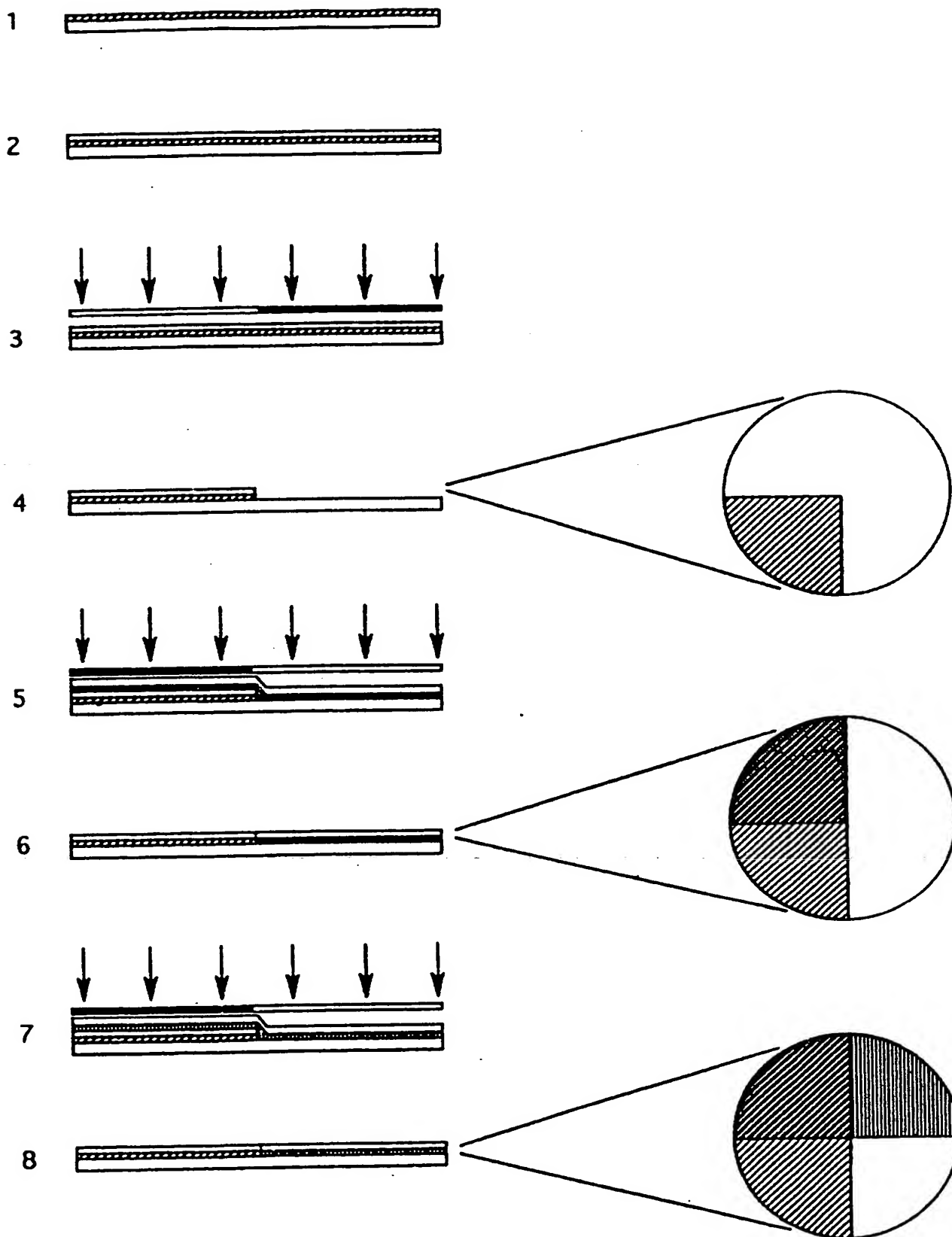
Fig. 3

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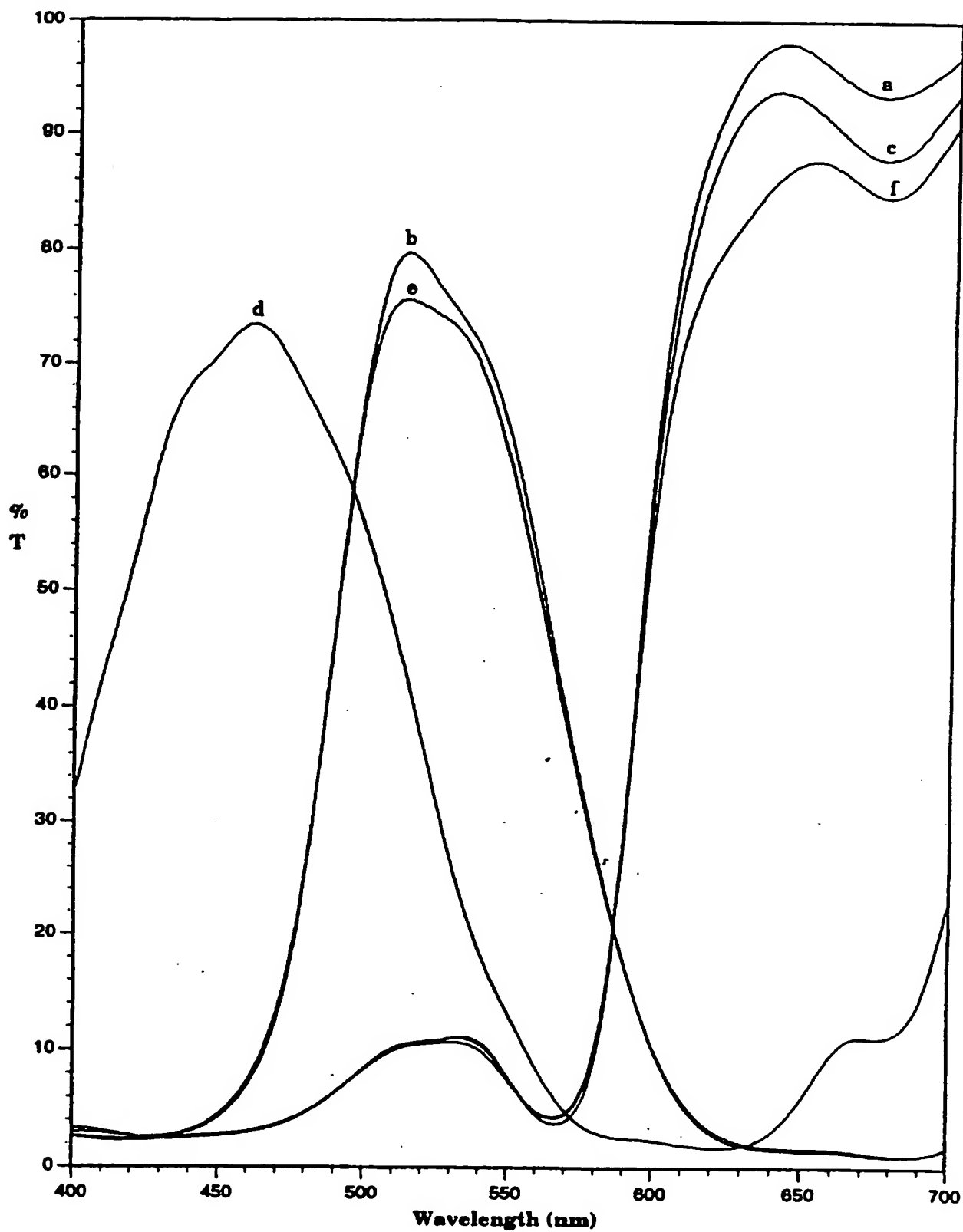
**Fig. 4**

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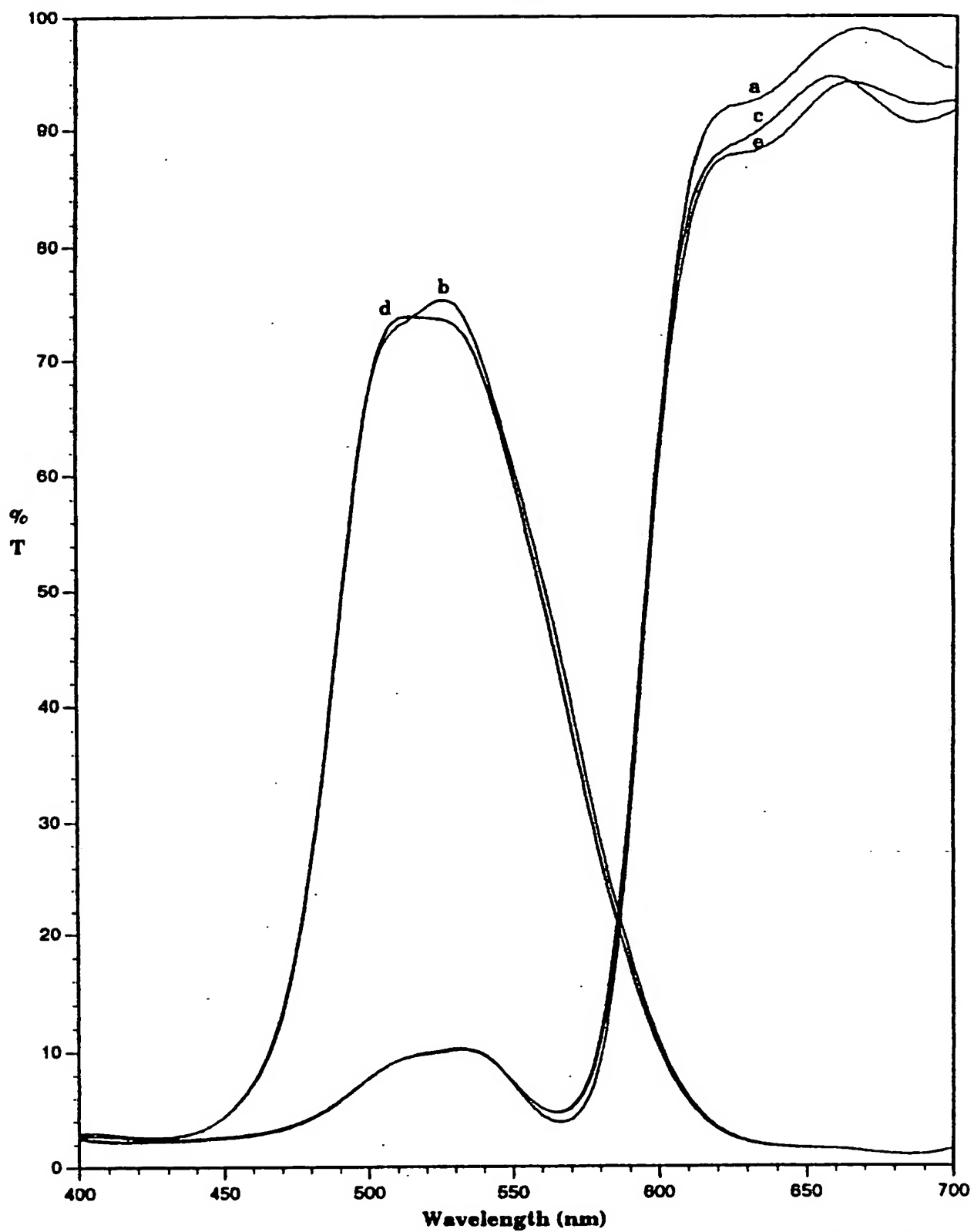
*Fig. 5*

**Fig. 6**

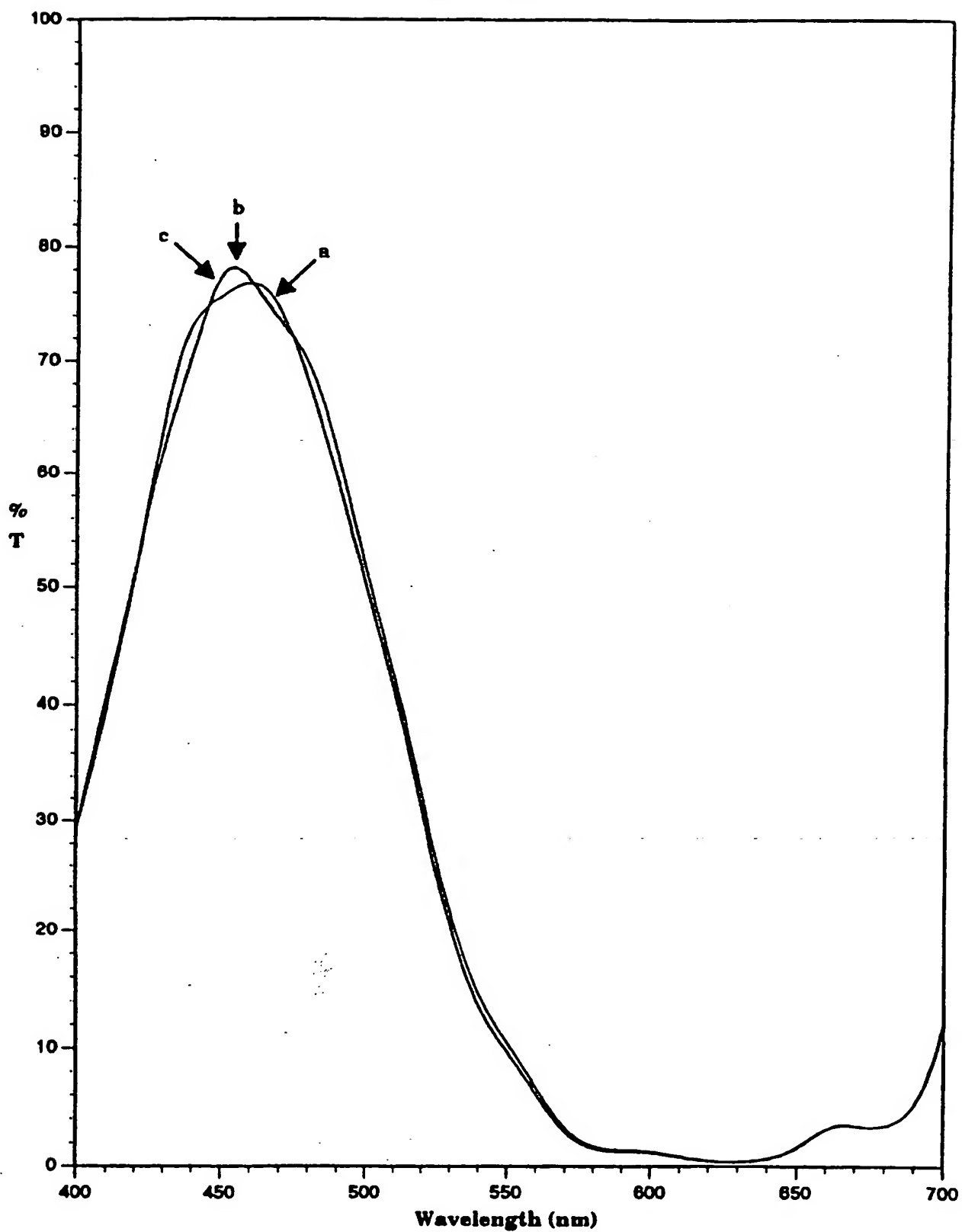
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*Fig. 7*

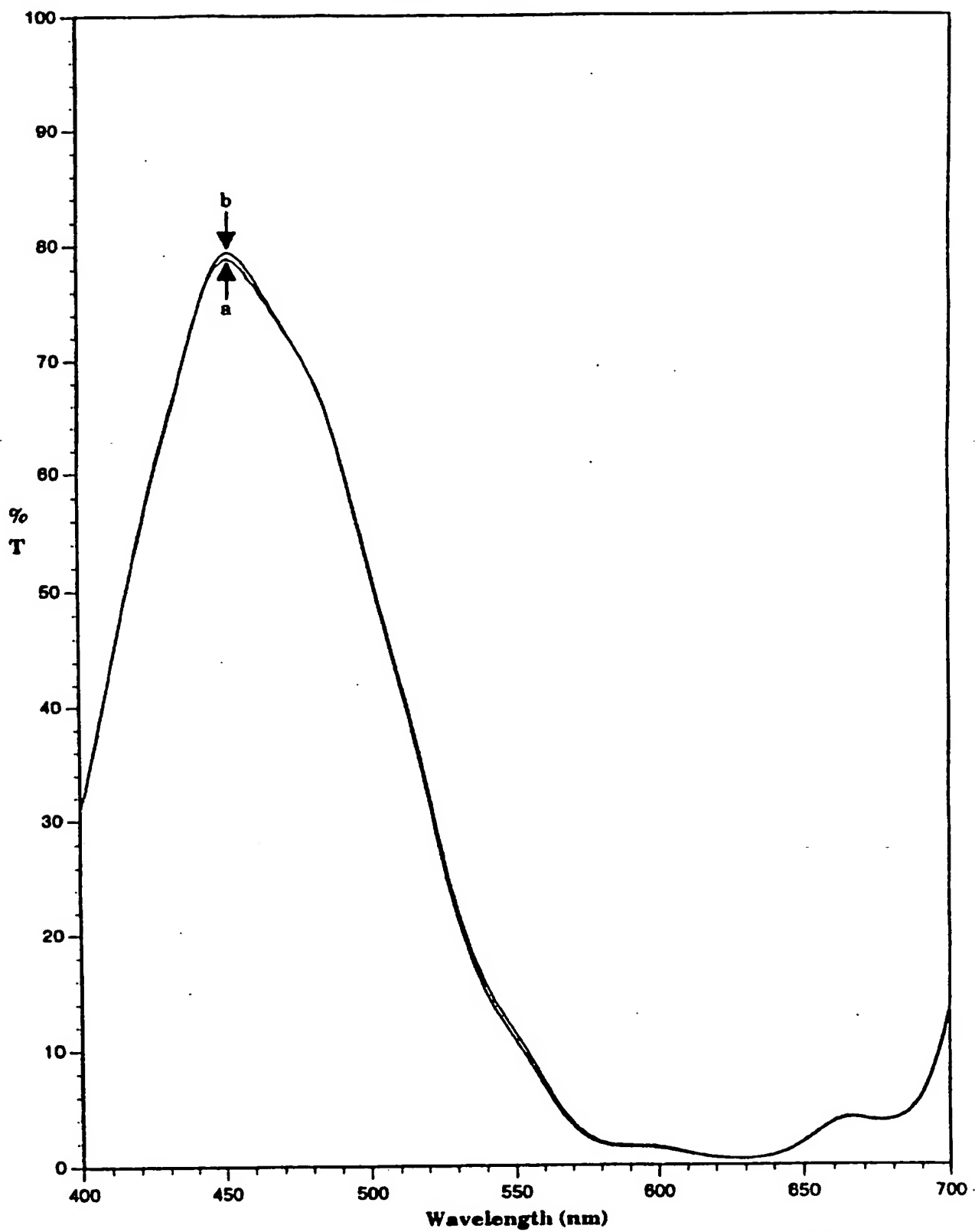
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*Fig. 8*

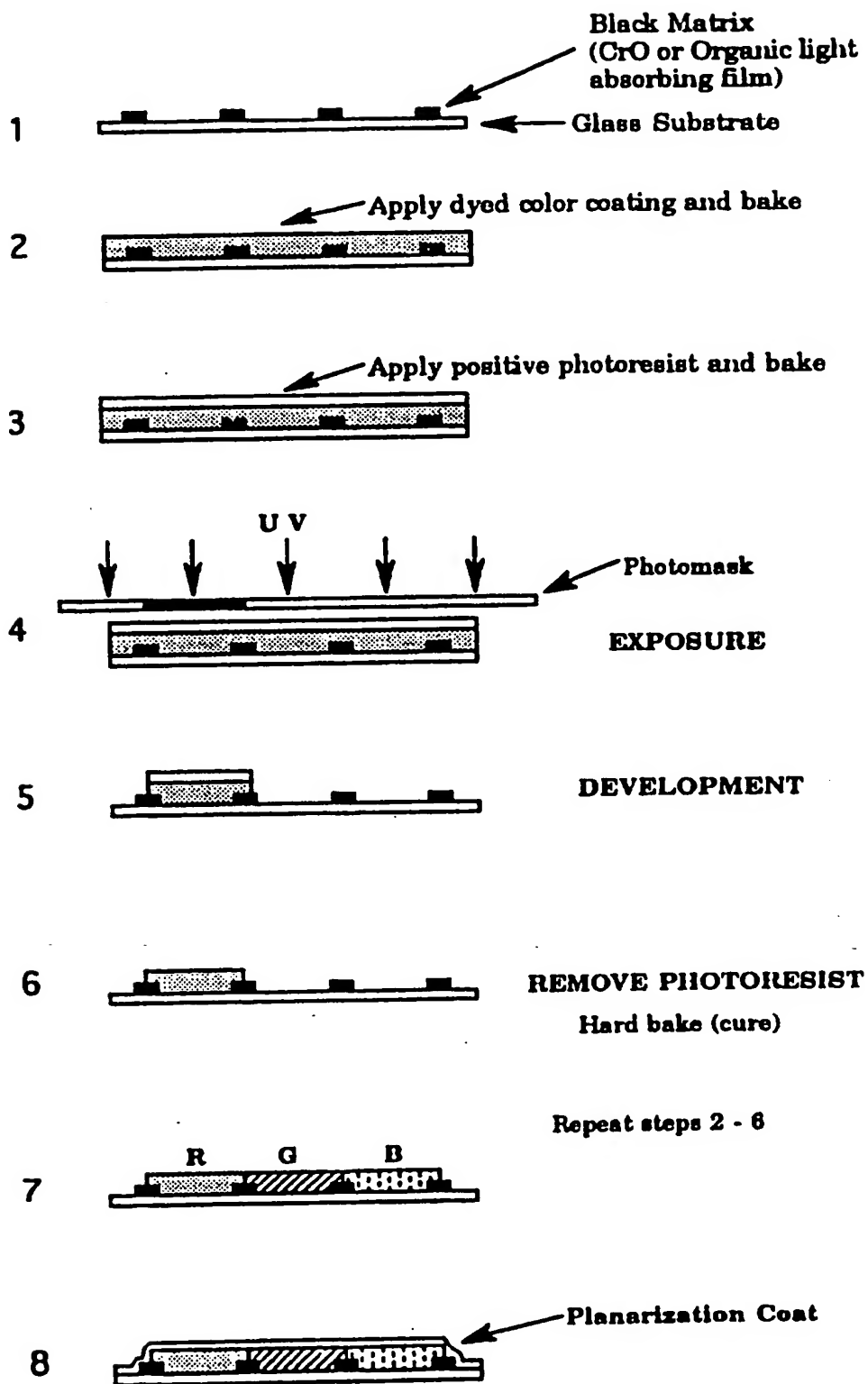
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**Fig. 9**

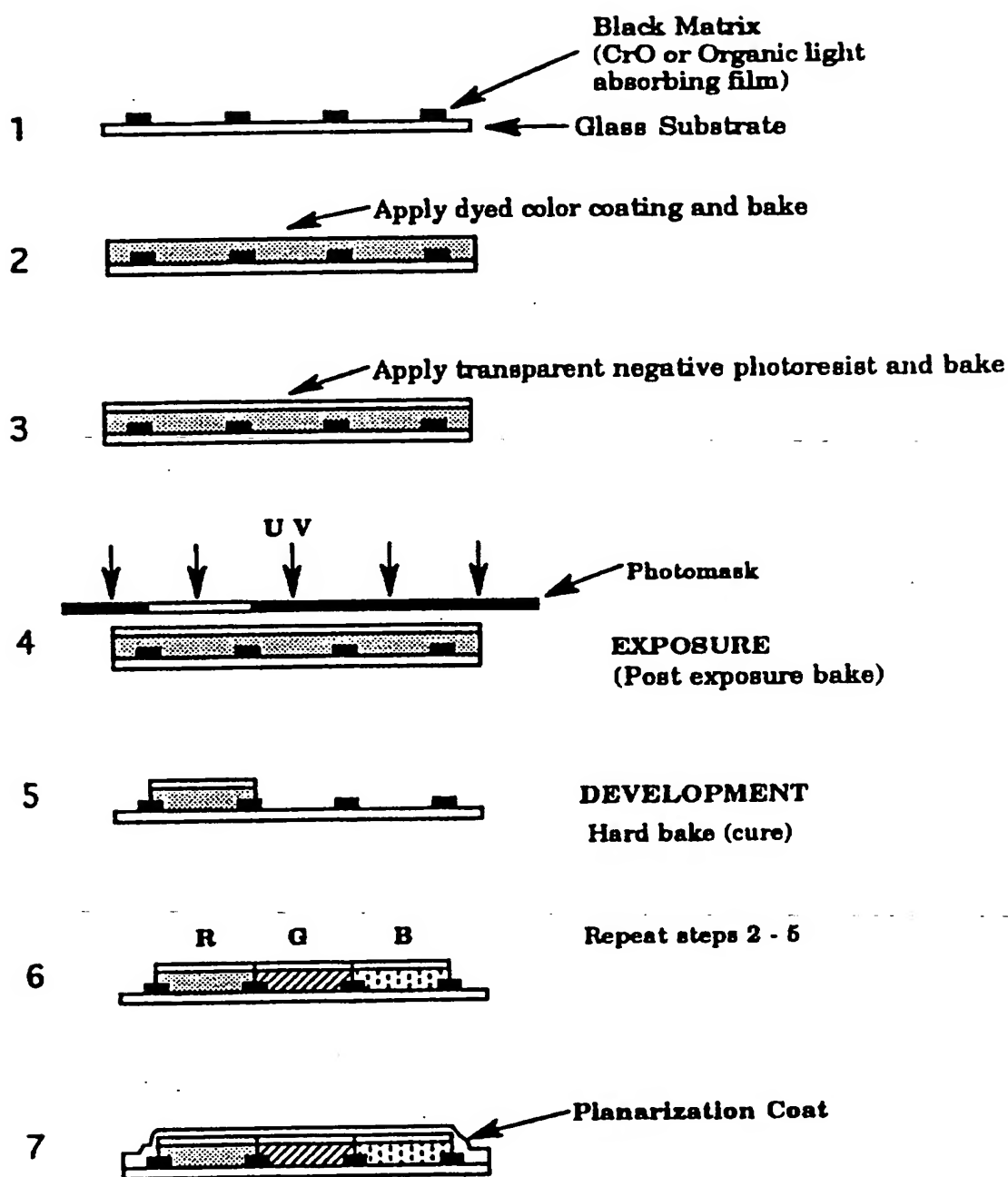
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**Fig. 10**

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*Fig. 11*

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**Fig. 12**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/05192

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : G03F 9/00; C09K 19/00; G03C 5/00, 5/56

US CL : 430/007, 020, 321

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 430/007, 020, 321

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,876,165 (BREWER et al.) 24 October 1989, see the claims.	1-10
Y	US, A, 5,236,793 (NISHIWAKI et al.) 17 August 1993, column 3, lines 2-59, column 5, lines 14-37, column 7, line 54 to column 8, line 21.	5, 10
X --- Y	JP, A, 57-4012 (CANON K.K.) 09 January 1982, see the Abstract.	1-3, 6, 7, 9 ----- 5, 8, 10

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

23 JULY 1996

Date of mailing of the international search report

05 SEP 1996

Name and mailing address of the ISA/US
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/05192

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	WO, A, 88/05180 (BREWER SCIENCE, INC.) 14 July 1988, page 2, lines 31-34, page 3, line 26, to page 4, line 9, page 3, lines 13-15, page 6, lines 1-29, page 9, line 28, to page 10, line 19, page 21, lines 4-8, page 26, line 7, to page 27, line 7.	1-4, 6, 7, 9 ----- 5, 8, 10
Y, P	US, A, 5,445,919 (WAKATA et al.) 29 August 1995, see the Abstract, column 2, lines 50-57, column 5, lines 13-47, column 6, lines 15-25 and 46-68, example 2.	1-10
Y	JP, A, 6-123967 (FUJI PHOTO FILM CO LTD) 06 May 1994, see the Abstract.	1-10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/05192

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/05192

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claims 1-7, drawn to an improvement in a process of making color filter elements by photolithography or by microphotolithography.

Group II, claim 8, drawn to a coating material including an anhydride modified copolymer grafted with a reactive crosslinking component and blended with a polyfunctional crosslinking component as the vehicle and a dye.

Group III, claims 9, 10, drawn to a color filter substrate with a patterned filter element thereon.

The inventions listed as Groups I-III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The coating material including a vehicle and a soluble light absorbing dye is not considered to be a special technical feature of the three groups of claims. Coating materials comprising a vehicle and a dye are conventional and well known in the art of making color filters. Applicant has not provided evidence of unexpected results for the coating material as claimed. Furthermore, the claims of Groups I and III do not require that the coating material in claim 8 be employed.